Metallocene-Based Functionalized Polyolefins as Compatibilizers in Polyolefin Nanocomposites

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ABSTRACT: This article reports a study of some functionalized polyolefins evaluated as compatibilizers in polyethylene nanocomposites. The functionalized polymers were prepared by direct metallocene-mediated copolymerizations of ethylene and a functional comonomer. The prepared nanocomposites were evaluated for mechanical and barrier property enhancement. A good combination of mechanical and barrier properties was obtained with the metallocene-based functionalized polyethylene. The toughness–stiffness balance was better than or comparable to that achieved with conventional functionalized polymers such as maleic anhydride grafted polyethylene. The results also indicated that these metallocene-based functionalized polyolefins, when used as compatibilizers, could have relatively higher molar masses and lower functionality than those of conventional post-reactor-modified compatibilizers, and so the drawbacks associated with the latter could be avoided. Their inherent properties could also further improve the final nanocomposite properties. This was attributed to the more homogeneous nature of metallocene-catalyzed polymers in comparison with post-reactor-modified products. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1094–1100, 2004

Key words: compatibilization; functionalization of polymers; organoclay; nanocomposites; polyolefins

INTRODUCTION

Research in the area of polymer nanocomposites is growing considerably within both academic and industrial sectors. The use of layered silicates to improve several different properties of a polymer is among the topics under investigation. The starting materials are different types of clays, which are dispersed in a polymer matrix so that, in the ideal case, the individual platelets in the layered structure are separated or delaminated. As a result, the surface area of the clay in contact with the polymer is several magnitudes greater than that with conventional reinforcement fillers. Among the expected improvements at low loading levels are mechanical strength and stiffness, increased temperature resistance, flame retardancy, and barrier properties.

Getting the clay-based fillers dispersed to nanodimensions in the polymer is, however, challenging. The *in situ* polymerization route, in which monomers are polymerized in the presence of layered silicates, was first achieved with nylon nanocomposites.[1,2] The same method was later used for polyethylene (PE) nanocomposites.[3,4] A second route for the preparation of nanocomposites is melt compounding, and this route is more commonly used for nonpolar polymers.[5] The clays are usually pretreated to be made organophilic. The use of post-reactor-modified functionalized polypropylene (PP) as the matrix polymer, for better compatibility with the organically modified layered silicate (OMLS), has been evaluated.[6–8] PP nanocomposites containing maleic anhydride (MAH) grafted PP oligomers used as compatibilizers, along with a nonpolar PP matrix polymer, have been prepared, and the resulting structures and properties have been discussed.[9–11] Ionic compatibilizers have also been studied with poly(ethylene terephthalate) and polyamide (PA) as matrix polymers.[12] MAH-modified polymers have been found to be effective as compatibilizers in preparing nanocomposites, and oligomeric species are preferred for better diffusion into the clay particles. These functionalized materials are usually produced in a second postreactor step and add to the cost of the final nanocomposite. There are other drawbacks associated with these products: the presence of free MAH and its negative effects on the composites and end applications, and the occurrence of either crosslinking (PE) or chain scission (PP) in the grafting step, producing broader property variations. Although oligomeric species are preferred for better intercalation, their low molar mass can worsen mechanical, thermal, and other properties, so their loading level has to be optimized. The content of functional groups can also affect barrier and mechanical properties, for example,

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TABLE I
Commercial Compatibilizers

Compatibilizer	PE-g-MAH (1)	PE-g-MAH (2)	PE-co-GMA
Description	MAH-grafted PE, Bynel CXA 4288 (DuPont)	MAH-grafted PE, Fusabond MX110D (DuPont)	GMA ethene copolymer, Bondfast E (Sumitomo)
Melt-flow rate (190°C, 2.1 kg), g/10 min	5.3	14.6	3.0
Functional group content (mol %)	0.1	0.4	2.4
M_w (g/mol)	123,000	41,500	122,500
T_m (°C)	125	120	101
Crystallinity (%)	44	53	37

M_w = weight-average molecular weight; T_m = melting temperature.

on account of their polar nature and reduced crystallinity.

Functional groups can be attached to polyolefin polymers through the polymerization of olefins in the presence of functional comonomers.[13,14] When such functionalized polyolefins prepared by single-site catalysts are used as compatibilizers, the grafting step can be avoided, and so the overall cost of the nanocomposites can be reduced. These polymers do not have the aforementioned drawbacks. In addition, because of their more uniform comonomer and molar mass distributions, they have higher density and crystallinity, which lead to better thermal and mechanical properties in comparison with conventional compatibilizers. We have previously reported that these kinds of copolymers perform well as compatibilizers in PE/PA blends[15] and in polymer/filler composites.[16] Improved adhesion to glass and metals[17–19] and compatibility with clay-based materials[20] have been demonstrated for hydroxyl, acid, or acid anhydride functionalized polyolefins prepared by copolymerizations.

In this study, we evaluated metallocene-based functionalized PE as the compatibilizer when preparing PE nanocomposites, and we compared the nanocomposite structure and properties with those obtained when postreactor MAH-grafted PE and a reactor-made polar copolymer via free-radical polymerization were used as compatibilizers.

EXPERIMENTAL

Commercial materials

The matrix polymer was a low-density polyethylene (LDPE) grade from Borealis (Porvoo, Finland) (melt-flow rate = 2 g/10 min at 190°C, 2.1 kg). The nanofiller was Cloisite 6A, an OMLS based on montmorillonite clay cation-exchanged with dimethyl di(hydrogenated tallow) ammonium salt, supplied by Southern Clay Products (Gonzales, Texas), Inc. For comparison with the metallocene-based functionalized PE grades, commercially available grafted and reactor-made copolymers were used. They are listed in Table I.

Metallocene-catalyzed preparation of functionalized PE copolymers

The preparation of PE-co-OH (3) is given as an example. PE-co-OH (1) and PE-co-OH (2) were prepared with a similar method; only the conditions and amounts of the reagents were changed (see Table II). 10-undecen-1-ol (7.5 mmol; Fluka, Buchs, Switzerland) was added to a polymerization reactor with a 1.0 dm^3 volume (Büchi, Uster, Switzerland) containing 600 cm^3 of moisture-free toluene and methylaluminoxane (10 wt % in toluene; Witco, Bergkamen, Germany), which corresponded to 60 mmol of aluminum. The mixture was stirred for 15 min, during which period the pressure of the reactor was increased to 1.5 bar with ethylene, and the solution was allowed to saturate with ethylene while the temperature was kept constant at 80°C. The copolymerization was initiated by the addition of 5.0 μmol of rac-ethylene bisindenyl zirconium dichloride (Witco), dissolved in moisture-free toluene, to the reactor. During the polymerization, ethylene was continuously fed into the reactor to maintain the total pressure at 1.5 bar. The reaction was terminated after 15 min, and the copolymer was precipitated by the addition of a solution of hydrochloric acid in ethanol. The polymer was filtered and washed with ethanol and acetone. The polymer yield was 19.3 g. The properties of the prepared copolymers are set out in Table III.

TABLE II
Preparation of Functionalized PE Copolymers

Name	PE-co-OH (1)	PE-co-OH (2)	PE-co-OH (3)
Comonomer in the feed (mmol)	15.0	7.5	7.5
Al-to-comonomer ratio (mol/mol)	4.0	4.0	4.0
Temperature (°C)	60	60	80
Polymerization time (min)	40	60	15
Yield (g)	9.7	11.7	19.3

TABLE III
Properties of Metallocene-Catalyzed Functionalized PE Copolymers

Name	PE-*co*-OH (1)	PE-*co*-OH (2)	PE-*co*-OH (3)
Functional group (OH) content (mol %)	1.0	0.3	0.3
M_w (g/mol)	74,700	98,400	52,700
M_w/M_n	2.6	2.8	2.1
T_m (°C)	126	129	131
Crystallinity (%)	53	59	65

M_w = weight average molecular weight; M_n = number-average molecular weight; T_m = melting temperature.

Nanocomposite preparation

The nanocomposites were produced by compounding of the LDPE matrix polymer, an organically modified nanofiller, and optionally the compatibilizer in a DSM laboratory corotating twin-screw extruder. The extruder had a volume of 16 cm³ and a screw length of 150 mm. The neat polymer was also extruded on its own as a reference sample. All formulations included 0.1 wt % Irganox 1010 as a stabilizer. The mixing temperature was 170°C, and the screw speed was 65 rpm. After 3 min of blending, the extrudate was directly injection-molded with a DSM mini-injection-molding unit into tensile test bars. The injection-molding temperature was 170°C, and the mold temperature was set at 50°C. The test bars were used subsequently for determining the mechanical properties and for electron microscopy analysis. Some of the extrudate was collected as strands and made into the form required for testing other properties.

Polymer characterization methods

The grafted MAH content in the commercial compatibilizers was calculated as follows. The total MAH was analyzed by the dissolution of the polymer in xylene followed by an acid–base titration; the free MAH was analyzed by extraction from the polymer solution with isopropyl alcohol and by acid–base titration of the extract. The grafted MAH content was then obtained by the subtraction of the free MAH content from the total MAH content. The glycidyl methacrylate (GMA) content was calculated from the mass percentage of 12% provided by the supplier.

The functional group contents of the metallocene-catalyzed compatibilizers were calculated from ¹H-NMR spectra measured from solutions in deuterated 1,1,2,2-tetrachloroethane at 125°C with a Varian Gemini 2000 300-MHz NMR spectrometer (Palo Alto, CA). The PE equivalent molar masses of the compatibilizers were determined with a polystyrene-based universal calibration method on a Waters Alliance GPC 2000 (Milford, MA) or Waters 150C gel permeation chro-

matograph at 140 or 135°C. 1,2,4-Trichlorobenzene was used as an eluant.

The melting and crystallization characteristics of the compatibilizers as well as the nanocomposite samples were analyzed on a Mettler TA820 differential scanning calorimeter (Columbus, OH) as follows. The samples were melted at 180°C for 5 min and then cooled from 180 to 0°C at a rate of 10°C/min; this was followed by heating from 0 to 180°C at the same rate. Exceptionally, the functionalized PE copolymers were heated to 150°C instead of 180°C. The degree of crystallinity was calculated in relation to the heat of fusion of perfectly crystalline PE (i.e., 290 J/g).

The melt flow rate of the compatibilizers was measured according to ISO 1133.

On the compounded samples, the tensile modulus, tensile strength, and elongation at break were measured according to ISO 527, specimen type 1BA, except that the specimen thickness was 1.5 mm. The Vicat softening temperature was measured according to ISO 306. The hardness (Shore D) was measured according to ISO 868. The barrier properties were measured on compression-molded films 100 μm thick molded at a temperature of 200°C, for oxygen permeability according to ASTM D 3985 and for moisture permeability according to ASTM F 1249.

Scanning electron microscopy (SEM) was used to study the dispersion of the OMLS in the matrix polymer in the compounded samples. Fractured surfaces of injection-molded specimens were scanned at a magnification of 10,000× on a JEOL JSM 5300 (Tokyo, Japan). In addition, approximately 30-μm-thick microtomed specimens were scanned at a magnification of 100× to detect the presence of agglomerates.

RESULTS AND DISCUSSION

All numerical data from the thermal, mechanical, and barrier property analysis of the samples are given in Table IV. SEM micrographs of some representative formulations are shown in Figures 1 and 2 at magnifications of 10,000× and 100×, respectively.

Nanocomposite morphology

In Figure 1, with no compatibilizer (Nanocomp 2), larger filler particles about 1 μm long and 0.5 μm thick can be seen, indicating nonexfoliated particles. When any of the compatibilizers were used, few if any larger particles were seen, and this illustrates their ability to improve exfoliation of the platelets. Nanocomposites with a grafted polymer compatibilizer show a smaller particle size and thus better platelet delamination (Nanocomp 3). When PE-*co*-GMA was used as the compatibilizer (Nanocomp 5), some larger particles of 25–50 μm remained in the composite, as shown in Figure 2 (Nanocomp 5). Although this polymer had the highest concen-

TABLE IV
Properties of the Nanocomposite Samples

|	Nanocomp 1: Pure LDPE	Nanocomp 2: LDPE + 5% nanofiller	Nanocomp 3: LDPE + 10% PE-g-MAH(1) + 5% nanofiller	Nanocomp 4: LDPE + 10% PE-g-MAH(2) + 5% nanofiller	Nanocomp 5: LDPE + 10% PE-co-GMA + 5% nanofiller	Nanocomp 6: LDPE + 10% PE-co-OH(1) + 5% nanofiller	Nanocomp 7: LDPE + 10% PE-co-OH(2) + 5% nanofiller	Nanocomp 8: LDPE + 10% PE-co-OH(3) + 5% nanofiller
Compatibilizer properties								
Functional group content in compatibilizer (mol %)			0.1	0.4	2.4	1.0	0.3	0.3
M_w of compatibilizer (g/mol)			123,000	41,500	122,500	74,700	98,400	52,700
T_m of compatibilizer (°C)			125.0	120.0	101	126.0	129.0	131.0
Crystallinity of compatibilizer (%)			44	53	37	53	59	65
Nanocomposite properties								
T_m (°C)	110	110	110	111	109	109	109	109
T_{cr} (°C)	98	97	99	99	102	101	102	99
Crystallinity (%)	40.5	40.5	41.5	41.0	42.0	40.5	41.5	42.5
Tensile modulus (MPa)	81	69	78	88.5	70	75	80	79
Tensile strength (MPa)	18.7 (15.5–20.5) (high deviation)	13.0	15.5	15.9	14.0	16.5	14.0	14.6
Elongation at break (%)	98	133 (high deviation, 88–189)	103	96	87	108	124	140
Vicat softening temperature (°C)	93	89	90	91	89	92	93	92
Hardness (Shore D)	46	32	44	45	45	47	49	48
Oxygen permeability (cc25 μm/m² 24 h bar)	7,187	3,735	3,530	3,603	4,025	3,739	3,484	2,854
Water vapor permeability (g 25 μm/m² 24 h)	2.3	2.1	2.2	2.1	2.7	2.0	1.6	1.6

M_w = weight-average molecular weight; T_m = melting temperature; T_{cr} = crystallisation temperature.
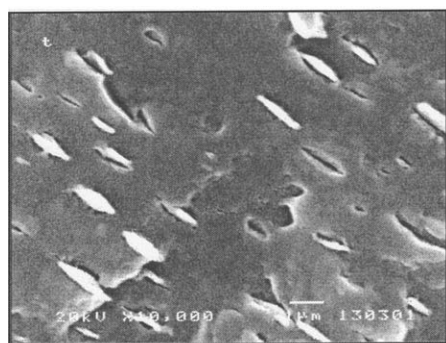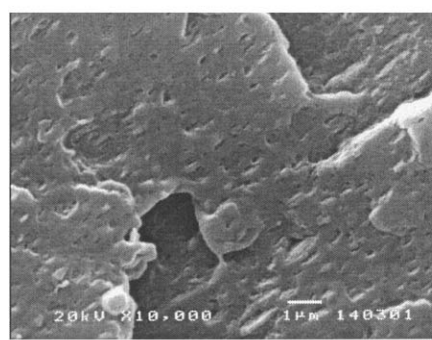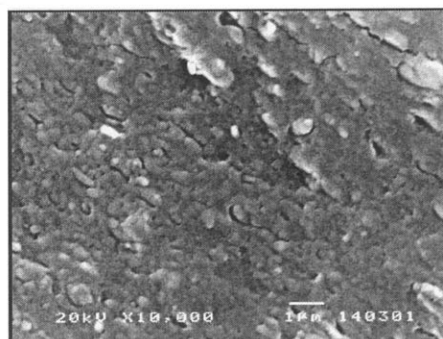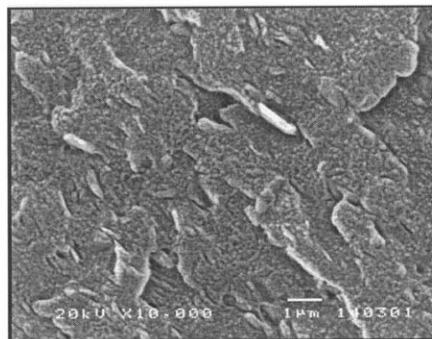
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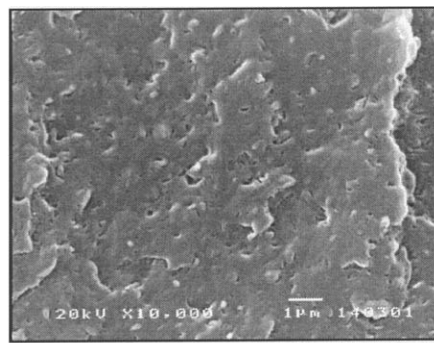
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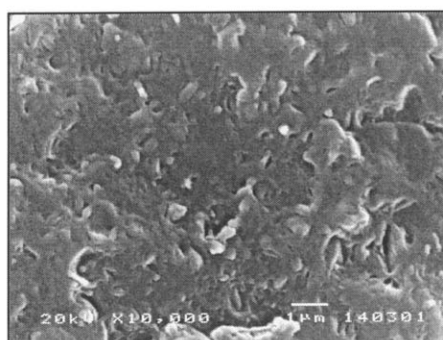
Nanocomp 5

Nanocomp 6

Nanocomp 7

Nanocomp 8

Figure 1 SEM micrographs of nanocomposite samples at a magnification of 10,000×.

tration of polar groups, its compatibilization efficacy appeared to be inferior to that of PE-*g*-MAH compatibilizers. On the contrary, when PE-*co*-OH was used as a compatibilizer, the composite morphology resembled that when PE-*g*-MAH was used. From these micrographs, we can conclude that the compatibilization effect of PE-*co*-OH is comparable to that of PE-*g*-MAH.

Thermal properties

No major influence of the layered silicate was seen on the melting and crystallization characteristics; the property values for the nanocomposite samples were in agreement with the thermal properties of the neat polymer and compatibilizers used. Layered silicates can act as nucleating agents, and the slight increase in the crystallization temperature is an indication of this.

Mechanical properties

The addition of the nanofiller to LDPE led to clearly reduced mechanical strength (Nanocomp 2). The Vicat softening temperature and hardness were clearly reduced in comparison with the base polymer. The two
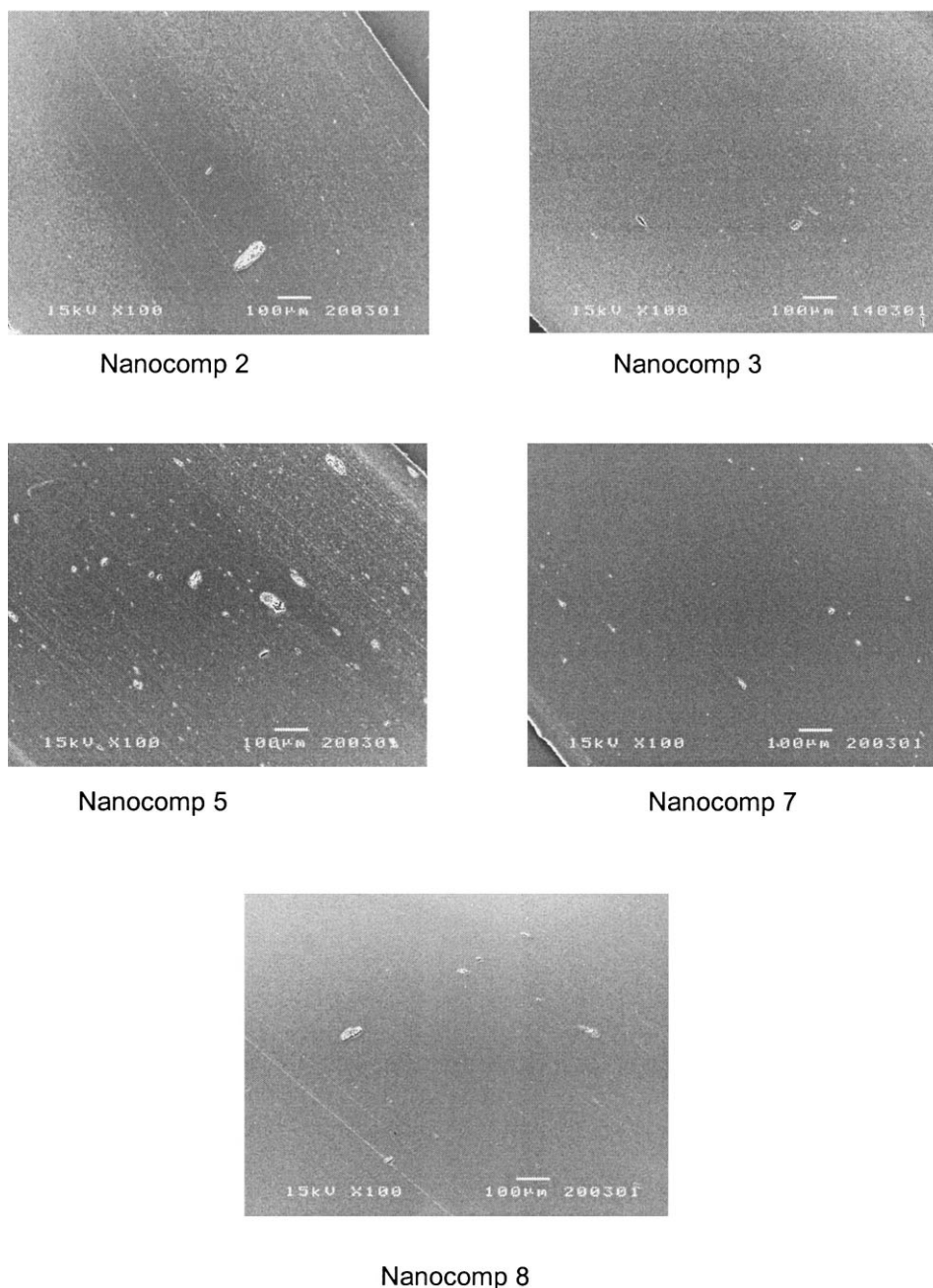
Figure 2 SEM micrographs of nanocomposite samples at a magnification of 100×.

samples containing the PE-*g*-MAH compatibilizers differed in stiffness. The compatibilizer with the higher MAH content and lower molar mass gave a better combination of properties, as expected. However, the individual effect of each of these variables cannot be analyzed from these two formulations alone. PE-*co*-GMA used as a compatibilizer did not improve the properties; instead, the inherent properties of this polymer were probably transferred to that of the composite. The PE-*co*-OH copolymers gave improved tensile properties comparable to or even better than those of PE-*g*-MAH. Thus, better toughness, as

indicated by the elongation at break together with the good tensile modulus values, indicates a better toughness–stiffness balance obtained with these polymers. The Vicat softening temperature and hardness values were also somewhat improved in comparison with those from the PE-*g*-MAH polymers. Among the three samples with PE-*co*-OH as the compatibilizer, no positive effect was observed with a higher functional group content, that is, Nanocomp 6 versus Nanocomp 7 and Nanocomp 8. Previous studies have shown that even though polar functionality is required, a high content can weaken compatibility between the matrix

polymer and the compatibilizer and consequently affect exfoliation negatively.[11] The associated lower crystallinity may also contribute to this result. For MAH-grafted polymers used as compatibilizers, a lower molar mass is expected to give better exfoliation on account of more facile diffusion into the layered silicates. The difference in the molar mass in PE-*co*-OH (2) and PE-*co*-OH (3), when the functional group content was the same, did not give rise to mechanical property differences. Within this study, changing the content of the OH functionality or molar mass did not seem to have an effect on the mechanical properties of the relevant composites.

Barrier properties

The oxygen permeability of the base polymer was reduced with filler incorporation, even without a compatibilizer. The numerical values obtained were in the same range, although a somewhat higher permeability value was seen with the PE-*co*-GMA polymer as a compatibilizer (Nanocomp 5). Among the three samples with PE-*co*-OH compatibilizers, the lowest permeability was seen with PE-*co*-OH (3), and this could be due to the lower molar mass, giving better exfoliation, and possibly also due to its crystallinity. The inherent moisture barrier of the matrix polymer was not further improved for most of the formulations. As expected, it worsened when the low-crystallinity PE-*co*-GMA polymer was used as a compatibilizer (Nanocomp 5). Two of the PE-*co*-OH polymers were clearly better than the rest. The reason for the poorer performance of PE-*co*-OH (1) could be attributed to the higher OH-group content in this compatibilizer and lower crystallinity.

CONCLUSIONS

A good combination of properties, mechanical and barrier, was obtained with the metallocene-based functionalized PE polymers as compatibilizers. When MAH-grafted polymers were used as compatibilizers, better exfoliation and thus nanocomposite properties were expected when the molar mass was low and the MAH content was adequate. This correlation does not necessarily hold in the case of metallocene-based functionalized PE compatibilizers. For these, other structural features such as the comonomer distribution, molar mass distribution, crystallinity, and crystalline structure could also be influencing the final nanocomposite properties. They could influence compatibility with both the inorganic filler and the matrix polymer; in addition, the inherent properties of these polymers used at the concentration of this study (10 wt %) could affect the final composite properties. For instance, the expected nar-

rower comonomer distribution for this type of polymer suggests that a lower functional group content than that of grafted polymers would be sufficient for good compatibilization. Additionally, possible differences due to the narrow molar mass distribution of these metallocene-based functionalized polymers, in comparison with the broader molar mass distribution in grafted PE polymers on account of an accompanying crosslinking reaction, should be considered.

The results of this study thus indicate that when metallocene-catalyzed functionalized polyolefin polymers are used as compatibilizers, nanocomposite properties similar to or better than those with MAH-grafted polyolefins can be obtained. The results also indicate that these materials when used as compatibilizers can have relatively higher molar masses and lower functionality than those of conventional post-reactor-modified compatibilizers, and consequently the drawbacks associated with the latter can be avoided.

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